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BEHAVIOUR OF CHEMICAL SPECIES UNDER REDUCING CONDITION IN A SUBAQUEOUS SOILS COLUMN

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ABSTRACT: In order to model the transport of multicomponent species including Mn^{2+} and Fe^{2+} from reduced layer to oxidized layer similar to paddy field condition, a preliminary column experiment was carried out. To reproduce actual paddy field conditions, the upper part of the column was filled with the soil taken from the paddy field and fine granite soil was filled in the lower soil of column. The experimental results showed that *ORP* (Oxidation Reduction Potential) rapidly decreased for first two days after the beginning of this experiment, and then showed a constant value. NO_3^- concentration in plow layer rapidly decreased due to the denitrification. On the other hand, the concentrations of dissolved Mn^{2+} and Fe^{2+} gradually increased after *ORP* achieved to a steady value, and they kept constant concentrations for 30 days.

INTRODUCTION

Oxidation and reduction processes play an important role on the spatial distribution of chemical species, for example O_2, NO_3^-, Mn^{2+}, and Fe^{2+} in soil. As an example of the redox environment in subsurface, Figure 1 shows a scheme of chemical species in paddy field condition. In plow layer of paddy fields, sequences of reduction reaction occur by heterotrophic activities of bacteria. After the dissolved oxygen is consumed by aerobic microorganisms, Mn- and Fe-oxides contained in soil matrix are reduced in order. When Mn^{2+} and Fe^{2+} dissolved during the infiltration through the plow layer (reduced layer) reach an oxidized layer below the plow layer, they are reprecipitated as Mn- and Fe-hydrolysis-oxides, respectively. Therefore, it is important to understand the physical, chemical, and biological processes of the species in a subsurface environment.

In recent years, different approaches for the simulation of transport processes involved in chemical reaction have been achieved (e.g., Rubin 1983; Kinzelbach et al. 1991; Matsunaga et al. 1993; Lensing et al. 1994). For example, Kinzelbach et al. (1991) have developed a model of microbial denitrification processes. Lensing et al. (1994) have modeled biologically mediated redox process which includes Mn(Ⅳ)-reduction and Fe(Ⅲ)-reduction. However, since Mn- and Fe-oxides are dissolved under reduction condition, cation exchange reaction including Mn^{2+} and Fe^{2+} should be taken into consideration in such kind of models.

In this study, to develop a model on the transport of multicomponent including the cation exchange of Mn^{2+} and Fe^{2+}, a preliminary column experiment was carried out. Based on the experimental results, the mechanism of multicomponent solute transport under redox condition was discussed.

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Note: Discussion on this paper is open until December 25, 1999.

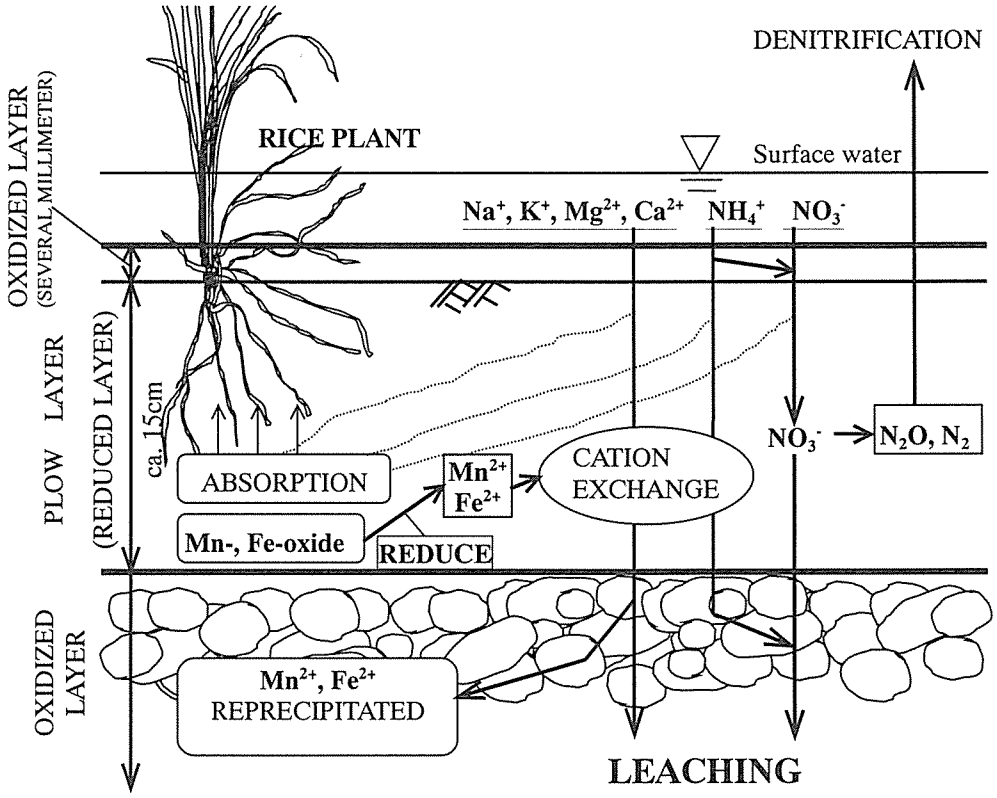

Fig. 1 Scheme of chemical species in paddy field condition

COLUMN EXPERIMENT

Experimental Procedure

Figure 2 illustrates experimental column equipment. Actual paddy field soil was filled from surface to 50 cm depth as plow layer (reduced layer). Fine granite soil was used from 50 cm depth to 100 cm as oxidized layer. After the column was filled with these soils, water was introduced in the column. The concentrations of chemical species in the water is shown in Table 1. To reproduce the redox condition similar to actual paddy field condition, water level was kept constant at about 5 cm.

Water samples were analyzed for Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, NH_4^+, and NO_3^-. pH, EC (electrical conductivity), and *ORP* were also measured. Water samples were collected by porous cups. These setting depth is shown in Fig. 2.

Experimental Results

Figure 3 shows *ORP* values, NO_3^-, Mn^{2+} , and Fe^{2+} concentrations at depth 5, 15, 25, 35, 45, and 65 cm with time. *ORP* values rapidly decreased for first two days, after that reached at stable values in the range of –0.2 to –0.3 V (depth of 5, 15, and 25cm). *ORP* values shows a rapid decrease at depth 5cm, compared with the deeper sites (depth 15 and 25 cm). *ORP* values at depth 35 and 45 cm showed unstable values with time, because of the insufficient contact between Pt-electrode and pore water. On the other hand, *ORP* values at 65 cm showed constant about 0.4 V.

Table 1 Concentrations of injection water and background concentrations in soil column

	Injection water	Background pore water (0 ~ 50 cm)	Background pore water (50 ~ 100 cm)
	meq l^{-1}	meq l^{-1}	meq l^{-1}
Na^+	0.70	3.81	3.61
K^+	0.15	0.47	0.15
Mg^{2+}	0.75	2.52	1.62
Ca^{2+}	3.02	7.44	3.63
Mn^{2+}	$4.0*10^{-3}$	$1.4*10^{-2}$	$1.2*10^{-2}$
Fe^{2+}	$9.7*10^{-3}$	$5.1*10^{-2}$	$8.1*10^{-2}$
NH_4^+-N	$3.2*10^{-3}$	$6.1*10^{-2}$	$4.0*10^{-2}$
NO_3^--N	0.20	4.84	4.46
pH	7.65	6.48	6.55
EC	0.44 mS cm^{-1}	1.49	0.96
ORP	0.25 V	0.32	0.36

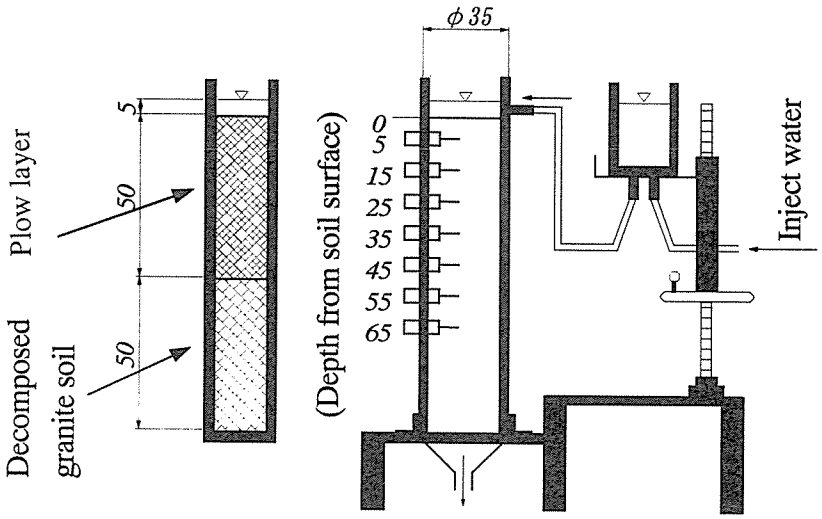

Fig. 2 Experimental column equipment

Next, as seen in Fig. 3, Mn^{2+} and Fe^{2+} concentrations were found to increase about for a month, after both concentrations showed constant. At the beginning of experiment, it can be seen that Mn-oxides is dissolved faster than Fe-oxides. Mn^{2+} and Fe^{2+} concentrations at depth 45 cm is higher than that at depth 5 cm. This is due to the dissolution of Mn- and Fe-oxides during the water infiltration through the plow layer (reduced layer). On the other hand, Mn^{2+} and Fe^{2+} concentrations at depth 65 cm were low. Since the reduced condition changed into the oxidized condition at 65 cm, Mn^{2+} and Fe^{2+} were reprecipitated as Mn- and Fe- hydrous oxides.

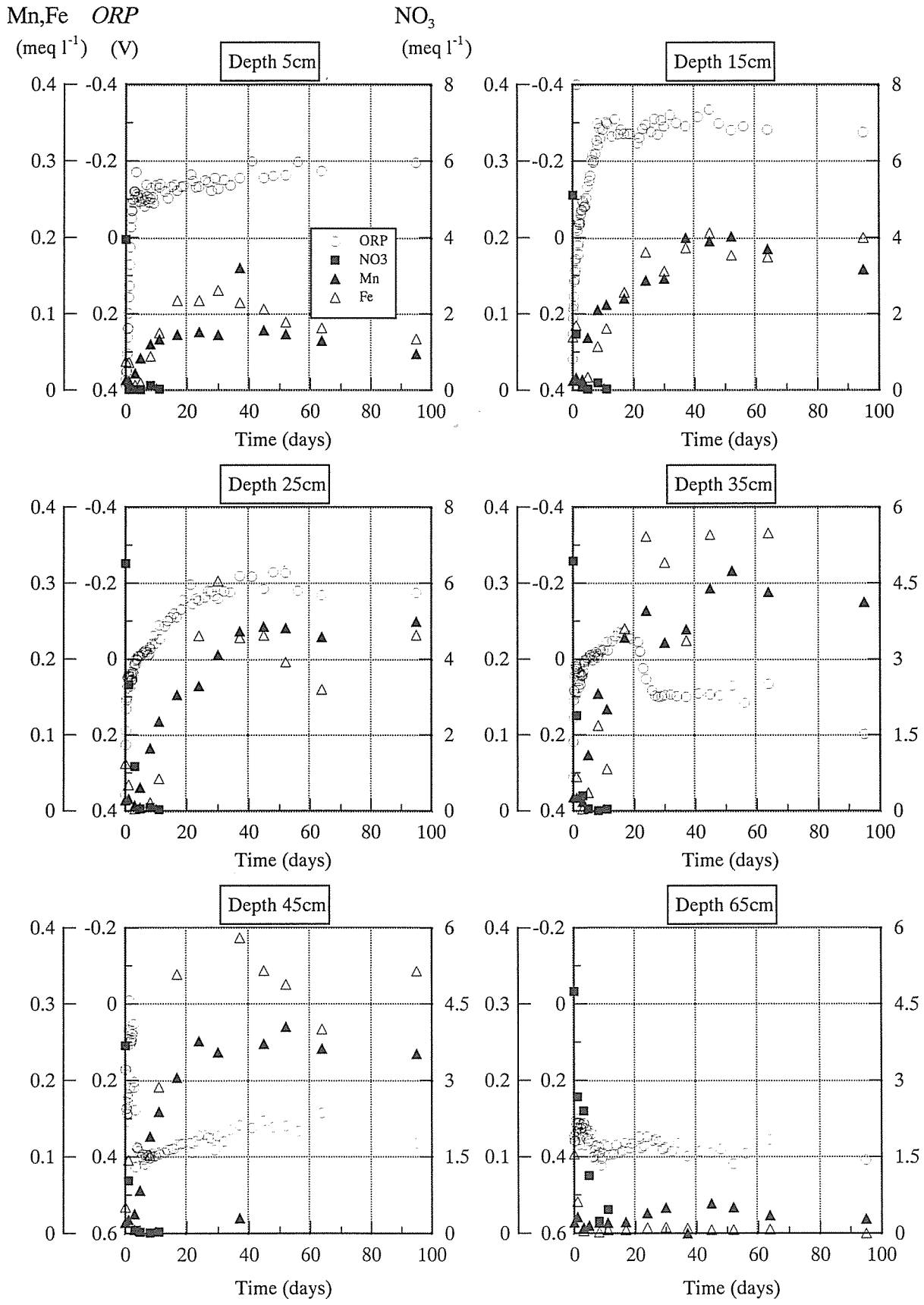

Fig. 3 *ORP* values and NO_3^-, Mn^{2+}, Fe^{2+} concentrations in pore water with time at different depth (5, 15, 25, 35, 45, and 65 cm)

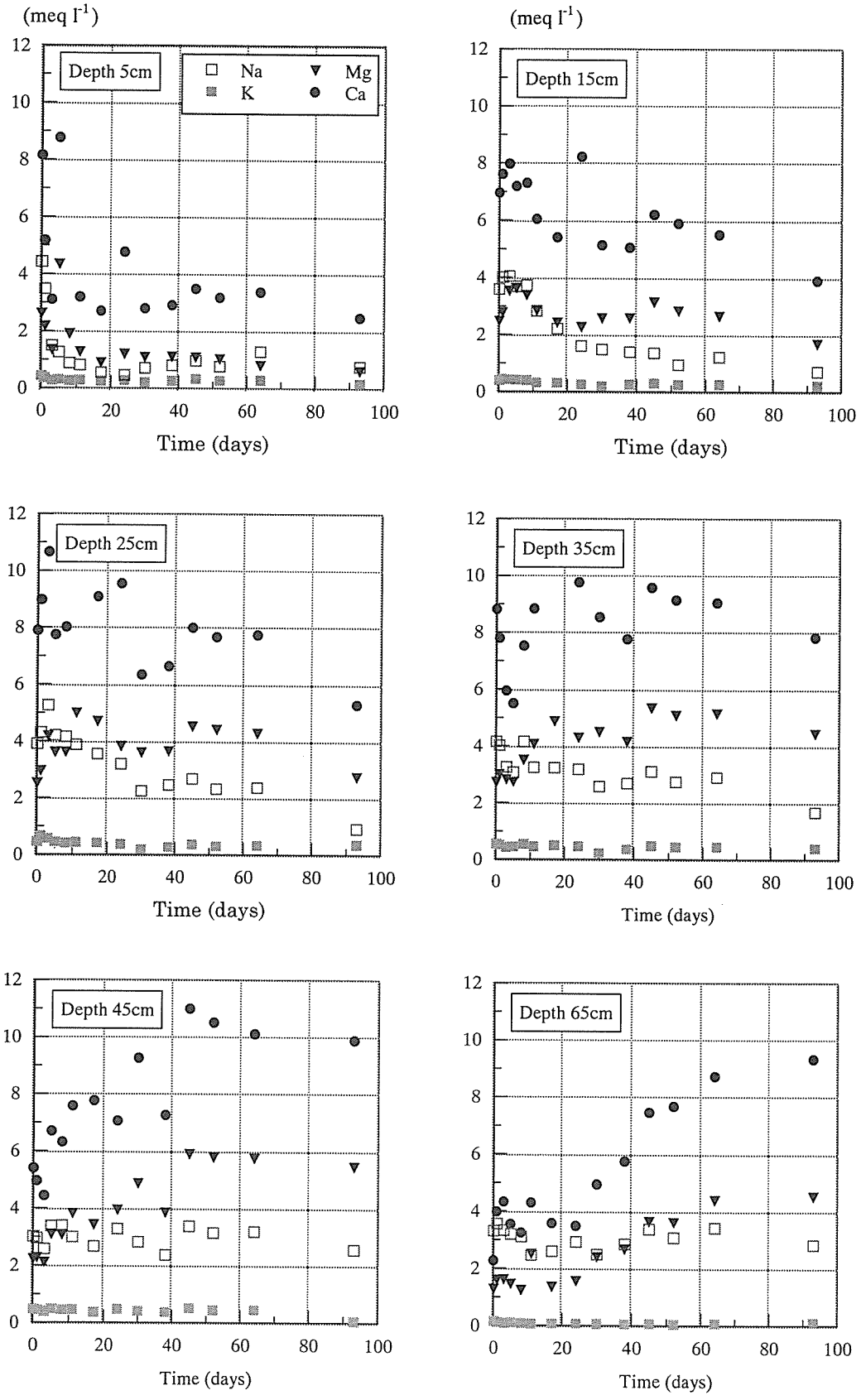

Fig. 4 Na^+, K^+, Mg^{2+}, and Ca^{2+} concentrations in pore water with time at different depth (5, 15, 25, 35, 45, and 65 cm)

NO_3^- concentration showed about 5 meq l^{-1} at any depth in the beginning of experiment. After that, its concentration in plow layer rapidly decreased due to the denitrification. On the other hand, NO_3^- concentration at depth 65 cm gradually decreased compared to their concentrations in plow layer. As seen from *ORP* variation in Fig. 3, denitrification doesn't occur in lower layer (50~100 cm) because of the existence of dissolved oxygen. It can be seen that the reason for decrease of NO_3 concentration is the water infiltration through the bottom of column.

Figure 4 shows Na^+, K^+, Mg^{2+}, and Ca^{2+} concentrations at 5, 15, 25, 35, 45, and 65 cm with time. Every cation concentration is higher than that of inject water at the beginning of experiment. After that, Na^+ concentration gradually decrease with time at depth 5, 15, 25, 35 cm. On the contrary, Mg^{2+} concentration gradually increases with time. Ca^{2+} concentration has a tendency to decrease from the depth 5 to 25 cm, whereas the concentration increases with time below the depth 45 cm. This is due to the desorption of Ca^{2+} by Mn^{2+} and Fe^{2+} and its infiltration. Momii et al. (1997) performed laboratory experiments at the continuous injection of water with high K^+ concentration. In that experiment, only cation exchange between K^+ (in liquid phase) and Ca^{2+} (in solid phase) occurred due to oxidized condition. However, our experiment was performed using dilute water under the redox condition. Surprisingly, Mn^{2+} and Fe^{2+} were detected in pore water in this experiment because dissolution of Mn^{2+} and Fe^{2+} from Mn- and Fe-oxides occurred. In this system, it is quite interesting to ascertain both effects of redox reaction and cation exchange reaction.

Figure 5 shows variation of pH in pore water with time at different depth. Initial pH values were in the range of 6.3 to 6.7 and increased with time at each depth. For one reason of increase of pH, reduction reactions in soils can be considered. The candidates as reduction reactions are as follows.

$$CH_2O + 2MnO_2 \Rightarrow 2Mn^{2+} + 3H_2O + CO_2 \quad (1)$$

$$CH_2O + 8H^+ + 4Fe(OH)_3 \Rightarrow 4Fe^{2+} + 11H_2O + CO_2 \quad (2)$$

where CH_2O is organic matter, microorganisms use CH_2O as their energy and use MnO_2, $Fe(OH)_3$ as electron acceptors. When reduction reaction proceeds (from left to right in the above equation), CO_2 is produced and pH increases.

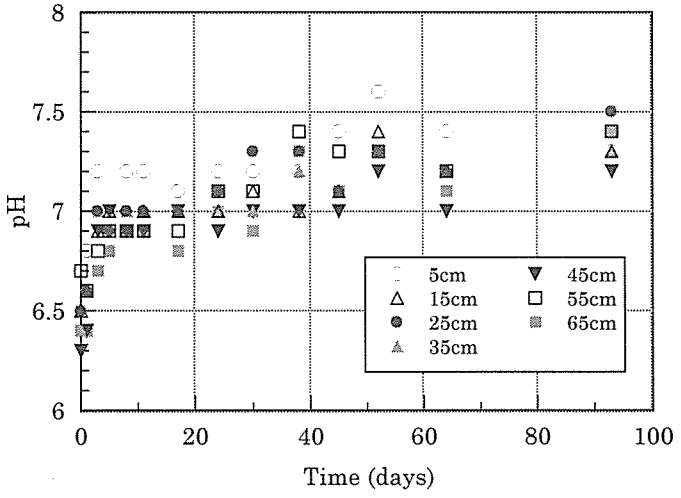

Fig. 5 Variation of pH in pore water with time at different depth (5, 15, 25, 35, 45, 55, and 65 cm)

Relationship between *ORP* and Fe^{2+} concentration

ORP under oxidized environments generally is higher than that under reduced environment, it has generally proved to be difficult to obtain a meaningful quantitative interpretation using *ORP* values. If we apply the Nernst equation to Fe(Ⅲ)-reduction reaction, the equation can be written as:

$$ORP(\mathrm{V}) = E^0 + \frac{RT}{nF}\ln\frac{[Fe^{3+}]}{[Fe^{2+}]} \tag{3}$$

where E^0 is the standard potential, or the potential with all substances present at unit activity at 25℃ and 1 atm (for Fe^{2+}/Fe^{3+} reaction, E^0 = +0.77), R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, n is the number of electrons transferred in the reaction (for this case, n =1), F is the Faraday's constant (9.64 10^4 C mol^{-1}). Differences between activities and molal concentrations are disregarded, $[Fe^{3+}]$ and $[Fe^{2+}]$ indicate molal concentrations. Substitute these values into Eq. (3), converts natural to base ten logarithms;

$$ORP(\mathrm{V}) = 0.77 + 0.059\log\frac{[Fe^{3+}]}{[Fe^{2+}]} \tag{4}$$

As for $[Fe^{3+}]$, consider equilibrium with the following dissolution-precipitation equation can be written as:

$$Fe(OH)_{3(s)} + 3H^+ \Leftrightarrow Fe^{3+} + 3H_2O \tag{5}$$

With equilibrium constant K, rewrite in logarithmic form;

$$\log K = 3\mathrm{pH} + \log[Fe^{3+}] = 4.78 \quad \text{at} \quad 25℃ \quad 1\mathrm{atm} \tag{6}$$

Substitute Eq. (6) into Eq. (4), *ORP* can be written using pH and Fe^{2+} concentration.

$$ORP(\mathrm{V}) = 1.06 - 0.177\mathrm{pH} - 0.059\log[Fe^{2+}] \tag{7}$$

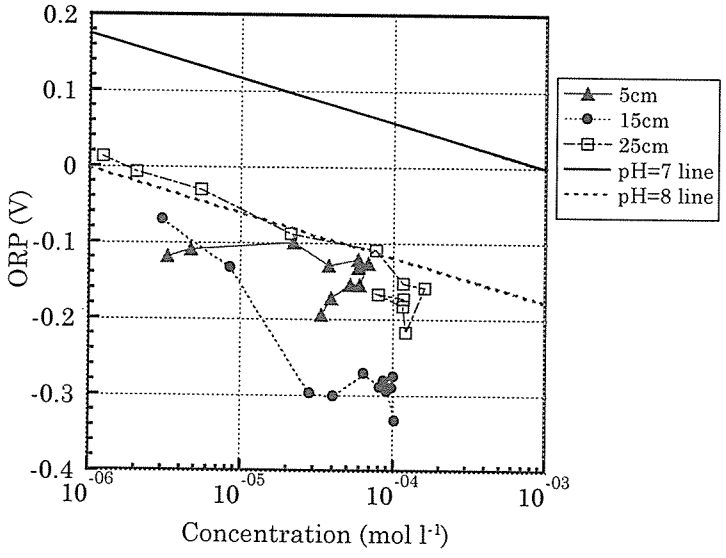

Fig. 6 Relationships between *ORP* and Fe^{2+} concentration

Figure 6 shows a comparison between experimental results of *ORP* and Fe^{2+} concentration and Nernst's formulation. Heavy line indicates Eq. (7) for pH=7, dashed line for pH=8. Experimental results agree approximately with theoretical results derived from Eq. (7).

CONCLUSION

In this study, to model the transport of multicomponent under redox condition similar to paddy field, a preliminary experiment was carried out. The major findings of experimental results is as follows:

1. NO_3^- concentration in plow layer rapidly decreased due to the denitrification.
2. In upper part of column (plow layer), *ORP* values rapidly decreased for first two days after the beginning of the experiment, and then showed a constant value. In lower part of column (fine granite soil layer), *ORP* showed a constant value (0.4 V) through the period of experiment because of oxidized condition.
3. The concentrations of dissolved Mn^{2+} and Fe^{2+} in plow layer gradually increased after *ORP* achieved to a steady state, and then showed constant concentrations. The dissolution of Mn^{2+} is faster than Fe^{2+}, representing sequential reduction processes. On the other hand, dissolved Mn^{2+} and Fe^{2+} concentrations at 65 cm were not almost detected. It is because Mn^{2+} and Fe^{2+} which dissolved during the infiltration through the plow layer reached an oxidized layer and were reprecipitated as Mn-, Fe-hydrous oxides.
4. To understand the mechanism of cation transport, other different reactions including cation exchange reaction must be considered. Furthermore, detailed interpretation are needed for changes of pH under redox reaction and cation exchange reaction. Moreover, it is necessary to develop the biogeochemical solute transport model with redox condition.

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